

Hexa-n-alkylcyclotrisiloxanes — synthesis, melting behaviour and polymerization

Gerhardus J. J. Out, Harm-Anton Klok^{a)}, Martin Möller**^{a)}

Department of Chemical Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

Dieter Oelfin

Institut für Makromolekulare Chemie, Hermann-Staudinger-Haus, Albert-Ludwigs-Universität, Stefan-Meier-Straße 31, 79100 Freiburg, Germany

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SUMMARY:

A homologous series of hexa-n-alkylcyclotrisiloxanes and poly(di-n-alkylsiloxane)s has been prepared with alkyl side groups varying in length between 4 and 10 carbon atoms. Melting transition enthalpies of the hexa-n-alkylcyclotrisiloxanes indicated a reversed odd-even effect, showing higher melting enthalpies for cyclotrisiloxanes with n-alkyl side groups with an odd number of carbon atoms. The melting behaviour of the heptyl- and octyl-substituted cyclotrisiloxanes was rather complex. Multiple melting transitions could be observed, which are presumably due to formation of a kinetically favoured crystalline phase next to the thermodynamically stable crystal modification. All hexa-n-alkylcyclotrisiloxanes could be polymerized by anionic or cationic ring-opening polymerization. The observation of longer polymerization times and formation of relatively larger amounts of cyclic byproducts in the case of hexadecylcyclotrisiloxane compared to hexaethylcyclotrisiloxane indicated that with increasing side group length, the anionic polymerization propagation rate constants k_p decreased, whereas the rate constants of depolymerization k_{dx} increased. Cationic polymerization with trifluoromethanesulfonic acid as the initiator, offered a way to enhance k_p relative to k_{dx} , which allowed the preparation of high-molecular-weight polymeric products in good yields even in case of cyclotrisiloxanes substituted with long n-alkyl groups. Apart from poly(dimethylsiloxane), poly(diheptylsiloxane) and poly(dinonylsiloxane), all poly(di-n-alkylsiloxane)s showed two crystalline phases which were separated by a crystal-crystal transition signifying melting of the side groups. Starting from poly(diethylsiloxane), poly(di-n-alkylsiloxane)s up to poly(dihexylsiloxane) displayed a hexagonal columnar mesophase as well, the stability of which increased with longer alkyl side groups. However, further elongation of the n-alkyl side groups to decyl appeared to destabilize the columnar mesophase. Poly(didecylsiloxane) only exhibited a metastable columnar mesophase in combination with the high-temperature crystalline phase.

Introduction

It has been well established that a number of organic-inorganic hybrid polymers, such as symmetrically substituted polysilylenes $(R_2Si)_n$, polyphosphazenes $((RO)_2PN)_n$ and polysiloxanes $(R_2SiO)_n$, are able to form a hexagonal columnar mesophase. Although this behaviour was first described for poly(diethylsiloxane) and

^{a)} Present address: Organische Chemie III, Makromolekulare Chemie, Universität Ulm, 89081 Ulm, Germany.

poly(dipropylsiloxane)¹¹, which have been investigated further since then²⁻⁶, main attention has been focused on polysilylenes⁷⁻⁹ and polyphosphazenes^{10,11}. Partially, this may be explained by the rather cumbersome synthesis of poly(di-n-alkylsiloxane)s, which have to be prepared by means of anionic or cationic ring-opening polymerization of hexa-n-alkylcyclotrisiloxanes. Moreover, poly(di-n-alkylsiloxane)s do not share the peculiar electronic properties exhibited e.g. by polysilylenes.

However difficult the preparation of poly(di-n-alkylsiloxane)s may be, the resulting polymers are evenly substituted and do not contain any crosslinking sites. Compared to polyphosphazenes, this makes them especially suitable model compounds to study the hexagonal columnar phase behaviour. Polysiloxanes substituted with ethyl to hexyl groups are highly crystalline materials, displaying two types of crystal phase and a hexagonal columnar mesophase, in which the polymer main chain and side groups are conformationally disordered^{6,12-14}. Symmetrical substitution of the polymer main chain by decyl groups leads to a destabilization of the columnar mesophase yielding a metastable liquid-crystalline phase, which could only be observed in combination with the partially disordered crystalline phase¹⁴.

This paper describes the synthesis, the properties and the ring-opening polymerization of hexa-n-alkylcyclotrisiloxanes. Beside a Japanese patent on hexa-n-alkylcyclotrisiloxanes, used as additives to enhance the processability and impact strength of polymers¹⁵, few details have been given yet on these materials^{13,16}. Systematic studies on the homologous series might help to elucidate the intriguing solid state behaviour of the homopolymers. Finally, the feasibility of ring-opening polymerization of long n-alkyl group-substituted cyclotrisiloxanes forms another feature, which has not been investigated so far.

Experimental part

Materials

Di-n-alkyldichlorosilanes have been prepared by means of hydrosilylation of 1-alkenes with dichlorosilane in the presence of hexachloroplatinic acid¹⁷. Zinc oxide (Merck, 99%) was used as received. Trifluoromethanesulfonic acid (Alfa) was freshly distilled under vacuum before use. Caesium hydroxide monohydrate (Aldrich) was dried in situ on a 5 mm × 5 mm stainless steel platelet under high-vacuum conditions at elevated temperatures before employing it as an initiator.

Monomers

Hexapentylcyclotrisiloxane: The synthesis of hexapentylcyclotrisiloxane is described as a typical example. A 500 mL three-neck flask equipped with reflux condenser, dropping funnel and stirring bar, was charged with 54 g (0,66 mol) of zinc oxide in 180 mL of ethyl acetate. Over a period of 1 h, a solution of 106 g (0,44 mol) of dichlorodipentylsilane in 120 mL of ethyl acetate was added, during which time the temperature of the mixture increased to approximately 50 °C. After the addition had been completed, the mixture was stirred for 1 h at room temperature. The white suspension was neutralized by pouring it slowly into 250 mL of a saturated sodium hydrogencarbonate solution under vigorous stirring. The suspension was filtered over a glass filter and the filtrate was extracted with diethyl ether. The combined organic phases were dried over Na₂SO₄. The crude condensation product was purified by means of distillation, using a vacuum-isolated 15 cm Vigreux column in combination with a Juvostat high-temperature oil bath, which allowed to reach constant bath temperatures as high as 320 °C. Isolated yield: 36 g (44%) hexa-

pentylcyclotrisiloxane (purity: 96,9% by gas-liquid chromatography (GLC); m.p. -7°C ; b.p. $180^{\circ}\text{C}/0,1\text{ mm}$; NMR (δ in ppm, relative to tetramethylsilane (TMS)): ^1H NMR (250 MHz): 1,46–1,26 (m, 12H, $(\text{CH}_2)_3$), 0,90 (t, $J = 6,6\text{ Hz}$, 6H, CH_3), 0,61 (t, $J = 7,9\text{ Hz}$, 4H, SiCH_2); ^{13}C NMR (62,9 MHz): 35,51 (C3), 22,36, 22,34 (C4, C2), 16,17 (C1), 13,95 (C5); ^{29}Si NMR (79,5 MHz): $-10,55$.

Hexahexylcyclotrisiloxane: Isolated yield 35% (purity: 93,4% (GLC)); m.p. 12°C ; b.p. $214^{\circ}\text{C}/0,1\text{ mm}$; NMR (δ in ppm, relative to TMS): ^1H NMR (250 MHz): 1,46–1,15 (m, 16H, $(\text{CH}_2)_4$), 0,88 (t, $J = 6,6\text{ Hz}$, 6H, CH_3), 0,58 (t, $J = 7,9\text{ Hz}$, 4H, SiCH_2); ^{13}C NMR (62,9 MHz): 32,98 (C3), 31,60 (C4), 22,63, 22,58 (C5, C2), 16,21 (C1), 14,12 (C6); ^{29}Si NMR (79,5 MHz): $-10,59$.

Hexaheptylcyclotrisiloxane: In case of heptyl- to decyl-substituted hexaalkylcyclotrisiloxanes, cyclic trimers were purified by repeated recrystallization. For this purpose, a 2 wt.-% solution in 2-propanol was cooled at a rate of $2^{\circ}\text{C}/\text{min}$ from $50-60^{\circ}\text{C}$ to a temperature at which the material started to precipitate, using a Huber thermostat. Yields of cyclic trimer were of the order of 10–45% with purities ranging between 92–99% as checked by solution ^{29}Si NMR (vide infra).

Isolated yield 14% (purity $>98\%$ (^{29}Si NMR)); m.p. 26°C ; NMR (δ in ppm, relative to TMS): ^1H NMR (250 MHz): 1,45–1,20 (m, 20H, $(\text{CH}_2)_5$), 0,90 (t, $J = 6,5\text{ Hz}$, 6H, CH_3), 0,60 (t, $J = 8,6\text{ Hz}$, 4H, SiCH_2); ^{13}C NMR (62,9 MHz): 33,31 (C3), 31,84 (C5), 29,09 (C4), 22,75, 22,71 (C6, C2), 16,24 (C1), 14,12 (C7); ^{29}Si NMR (79,5 MHz): $-10,58$.

Hexaoctylcyclotrisiloxane: Isolated yield 19% (purity $>98\%$ (^{29}Si NMR)); m.p. 40°C ; NMR (δ in ppm, relative to TMS): ^1H NMR (250 MHz): 1,45–1,20 (m, 24H, $(\text{CH}_2)_6$), 0,90 (t, $J = 6,8\text{ Hz}$, 6H, CH_3), 0,60 (t, $J = 8,0\text{ Hz}$, 4H, SiCH_2); ^{13}C NMR (62,9 MHz): 33,33 (C3), 31,98 (C6), 29,38 (C4), 29,28 (C5), 22,70 (C7, C2), 16,21 (C1), 14,11 (C8); ^{29}Si NMR (79,5 MHz): $-10,62$.

Hexanonylcyclotrisiloxane: Isolated yield 10% (purity $>98\%$ (^{29}Si NMR)); m.p. 44°C ; NMR (δ in ppm, relative to TMS): ^1H NMR (250 MHz): 1,45–1,20 (m, 28H, $(\text{CH}_2)_7$), 0,90 (t, $J = 6,5\text{ Hz}$, 6H, CH_3), 0,60 (t, $J = 8,6\text{ Hz}$, 4H, SiCH_2); ^{13}C NMR (62,9 MHz): 33,34 (C3), 31,97 (C7), 29,60 (C5), 29,45 (C4, C6), 22,72, 22,70 (C8, C2), 16,22 (C1), 14,11 (C9); ^{29}Si NMR (79,5 MHz): $-10,58$.

Hexadecylcyclotrisiloxane: Isolated yield 48% (purity 92% (^{29}Si NMR)); m.p. 51°C ; NMR (δ in ppm, relative to TMS): ^1H NMR (250 MHz): 1,46–1,18 (m, 32H, $(\text{CH}_2)_8$), 0,88 (t, $J = 6,8\text{ Hz}$, 6H, CH_3), 0,58 (t, $J = 8,0\text{ Hz}$, 4H, SiCH_2); ^{13}C NMR (62,9 MHz): 33,32 (C3), 31,96 (C8), 29,74 (C5, C6), 29,64 (C4), 29,41 (C7), 22,70 (C9, C2), 16,20 (C1), 14,11 (C10); ^{29}Si NMR (79,5 MHz): $-10,58$.

Polymerization

Polymerizations have been carried out in bulk either by anionic ring-opening polymerization using high-vacuum breakseal techniques, or by cationic ring-opening polymerization under argon.

In case of anionic polymerization, 3 g of hexa-*n*-alkylcyclotrisiloxane was azeotropically dried with toluene/dibutylmagnesium and sealed into an ampoule equipped with a breakseal. The monomer ampoule was attached to a reaction flask. A catalytic amount of a caesium hydroxide ($<1\text{ mg}$) was placed on a $5\text{ mm} \times 5\text{ mm}$ stainless steel platelet, transferred into the reaction flask and subsequently dehydrated by melting at 272°C under high vacuum. The steel platelet served as a means to protect the initiator from reaction with the glass. The system was subsequently sealed under high vacuum. By breaking the breakseal using the stirring bar, the monomer was transferred into the reaction vessel. Polymerization occurred at 150°C , the reaction times ranging between 1 to 2 h, during which time a gradual increase in viscosity was observed.

Trifluoromethanesulfonic acid was used as initiator for the cationic polymerization of hexaalkylcyclotrisiloxanes substituted with heptyl- to decyl-groups. A three-neck flask, equipped with an argon inlet, stirring bar, septum and connected via a valve to a vacuum line, was charged with 3 g of monomer. After melting at 50°C , the monomer was degassed twice, followed by addition of $1\text{ }\mu\text{L}$ of trifluoromethanesulfonic acid via the septum. Formation of high-molecular-weight polymer took place within 24 h at 50°C but the reaction mixture was normally allowed to stand for another 48 h at the same temperature before work-up.

The crude polymeric products were precipitated twice in refluxing ethanol, or in the cases of heptyl- to decyl-substituted polymers in refluxing 2-propanol, in order to remove oligomeric side-products and traces of the initiator. After fractionation in toluene/ethanol the polymer samples were dried in vacuum at 110 °C. ^1H and ^{13}C chemical shifts of the polymers are summarized in Tab. 1.

Tab. 1. ^1H and ^{13}C NMR chemical shifts δ relative to tetramethylsilane (TMS) of poly(di-n-alkylsiloxane)s (R_2SiO) $_n$ measured in CDCl_3 at 298 K. C^1 refers to the carbon atom attached to the polymer main chain

R	^1H NMR (250 MHz) (δ in ppm relative to TMS)	^{13}C NMR (62,9 MHz) (δ in ppm relative to TMS)
pentyl	1,43–1,18 (m, 12 H, $(\text{CH}_2)_3$), 0,89 (t, $J = 6,6$ Hz, 6 H, CH_3), 0,50 (t, $J = 7,9$ Hz 4 H, SiCH_2)	35,98 (C^3), 22,83 (C^2), 22,41 (C^4), 16,63 (C^1), 14,03 (C^5)
hexyl	1,46–1,18 (m, 16 H, $(\text{CH}_2)_4$), 0,89 (t, $J = 6,5$ Hz, 6 H, CH_3), 0,61–0,41 (m, 4 H, SiCH_2)	33,56 (C^3), 31,80 (C^4), 23,19 (C^2), 22,79 (C^5), 16,75 (C^1), 14,11 (C^6)
heptyl	1,46–1,17 (m, 20 H, $(\text{CH}_2)_5$), 0,89 (t, $J = 6,6$ Hz, 6 H, CH_3), 0,62–0,40 (m, 4 H, SiCH_2)	33,87 (C^3), 32,08 (C^5), 29,31 (C^4), 23,24 (C^2), 22,79 (C^6), 16,71 (C^1), 14,10 (C^7)
octyl	1,46–1,15 (m, 24 H, $(\text{CH}_2)_6$), 0,89 (t, $J = 6,6$ Hz, 6 H, CH_3), 0,60–0,40 (m, 4 H, SiCH_2)	33,96 (C^3), 32,12 (C^6), 29,66 (C^4), 29,63 (C^5), 23,26 (C^2), 22,79 (C^7), 16,72 (C^1), 14,09 (C^8)
nonyl	1,46–1,15 (m, 28 H, $(\text{CH}_2)_7$), 0,89 (t, $J = 6,6$ Hz, 6 H, CH_3), 0,59–0,42 (m, 4 H, SiCH_2)	33,97 (C^3), 32,09 (C^7), 29,96 (C^5), 29,75 (C^4), 29,63 (C^6), 23,27 (C^2), 22,76 (C^8), 16,72 (C^1), 14,10 (C^9)
decyl	1,46–1,14 (m, 32 H, $(\text{CH}_2)_8$), 0,88 (t, $J = 6,4$ Hz, 6 H, CH_3), 0,58–0,43 (m, 4 H, SiCH_2)	33,98 (C^3), 32,06 (C^8), 30,05 (C^5), 29,97 (C^6), 29,77 (C^4), 29,61 (C^7), 23,27 (C^2), 22,75 (C^9), 16,72 (C^1), 14,09 (C^{10})

Methods

Analytical gas chromatography (GLC) was performed on a Varian 3400 instrument, equipped with a DS 654 data station. A DB-5 capillary column was used (30 m \times 0,32 mm \times 0,25 μm) in combination with a flame ionization detector (FID). Injection: on column, injector temperature: 70 °C–100 °C/min–290 °C; column: 60 °C (3 min)–10 °C/min–290 °C; detector: 295 °C. Gas flow: 3 mL/min N_2 .

Gel-permeation chromatography (GPC) measurements have been carried out with toluene as solvent, using Waters microstyragel columns (pore sizes 10^5 , 10^4 , 10^3 , 10^6 Å). Molecular weights were determined through universal calibration^{18,19}. A dual detection system consisting of a differential refractometer (Waters model 410) and a differential viscometer (Viscotek model H502, UNICAL software) allowed the simultaneous determination of molecular weights, molecular weight distributions and intrinsic viscosities $[\eta]$.

Calorimetric measurements were performed on a Perkin-Elmer DSC-7 equipped with a PE-7700 computer and TAS-7 software at scan rates between 1 to 10 K/min. Sample weights were typically chosen between 1,5 and 5 mg. Transition entropies ΔS were calculated assuming equilibrium, i. e. $\Delta H = T \Delta S$ (ΔH representing the transition enthalpy and T absolute temperature). Cyclohexane,

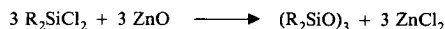
gallium and indium were used as the calibration standards. The onset of the recorded endotherm on heating was taken as the transition temperature.

Nuclear magnetic resonance (NMR) spectroscopy: Solution ^1H and proton decoupled ^{13}C NMR spectra were recorded on a Bruker AC 250 spectrometer at 250,1 MHz and 62,9 MHz, respectively, ^{29}Si NMR spectra were recorded on a Varian 400 WB spectrometer at 79,5 MHz. Relaxation times of 80 s were chosen in order to ensure near to complete relaxation of the ^{29}Si nuclei between successive scans. In all cases, CDCl_3 was used as solvent and TMS as a reference. The denotation C^1 refers to the carbon atom attached to the polymer main chain. Assignment of ^{13}C NMR resonances are based on 2D correlation experiments reported before on *n*-alkyl-substituted polysilylenes²⁰⁾.

Results and discussion

Synthesis

The hexa-*n*-alkylcyclotrisiloxanes were prepared in good yields by the reaction of the corresponding di-*n*-alkyldichlorosilanes with 1,5 equivalent amounts of zinc oxide¹⁶⁾.



The thermodynamically unexpected formation of the strained three-membered ring appears to be favoured kinetically at the heterogeneous contact with the finely dispersed zinc oxide particles. Purification by vacuum distillation allowed to isolate the cyclotrisiloxanes in high purity with the cyclotetrasiloxane as the major impurity to be detected by gas chromatography (GLC) and ^{29}Si NMR. The results are summarized in Tab. 2. As the presence of small amounts of the four-membered cyclosiloxanes does not interfere with the ring-opening polymerization, no further attempt has been made to improve the purity of the monomers.

Polymerizations have been carried out in bulk, either with caesium hydroxide as an anionic initiator or with trifluoromethanesulfonic acid as a cationic initiator. In order to exclude protic impurities stringently, high-vacuum breakseal techniques were employed for the anionic polymerization. Due to lower rates, the anionic polymerization reactions had to be carried out at 150 °C, whereas the cationic polymerizations proceeded smoothly at 50 °C. Yields, molecular weights, ratios of mass- to number-

Tab. 2. Properties of hexa-*n*-alkylcyclotrisiloxanes $(\text{R}_2\text{SiO})_3$

R	m. p. in °C	b. p. in °C/mmHg	Yield in %	Purity in %
pentyl	−7	180/0,1	44	96,9 ^{a)}
hexyl	12	214/0,1	35	93,4 ^{a)}
heptyl	26	—	14	> 98 ^{b)}
octyl	40	—	19	> 98 ^{b)}
nonyl	44	—	10	> 98 ^{b)}
decyl	51	—	48	92,2 ^{b)}

a) According to gas chromatography (GLC) analysis.

b) According to ^{29}Si NMR spectroscopy.

average molar masses and intrinsic viscosities from the highest molecular-weight fractions of the various poly(di-n-alkylsiloxane)s as measured in toluene, are summarized in Tab. 3.

With increasing length of the side groups, hexa-n-alkylcyclotrisiloxanes required progressively longer reaction times before high-molecular-weight polymers were obtained, and the onset of redistribution reactions occurred earlier with respect to the

Tab. 3. Yield, mass-average molar mass \bar{M}_w , ratio of mass- and number-average molar masses \bar{M}_w/\bar{M}_n and intrinsic viscosity of fractionated poly(di-n-alkylsiloxane)s as determined in toluene at 300 K

R	Yield in %	\bar{M}_w ^{a)} g/mol	\bar{M}_w/\bar{M}_n ^{a)}	$[\eta]$ ^{b)} dL/g	$[\eta]$ ^{c)} dL/g
pentyl	47	660 000	2,0	1,23	1,28
hexyl	42	1 330 000	1,8	1,93	1,83
heptyl	33	4 500 000 ^{d)}	1,2	—	2,47
octyl	22	440 000	1,2	—	0,96
nonyl	32	1 400 000	1,2	—	1,40
decyl	35	900 000	1,5	1,22	1,21

a) From gel-permeation chromatography according to universal calibration.

b) According to viscosity measurements in toluene at 298 K using an Ubbelohde device.

c) From online detection upon gel-permeation chromatography.

d) Data are near to the exclusion volume of the column.

overall conversion. Upon equilibration, both cationic and anionic polymerization ultimately leads to an equilibrium distribution of polymeric material and cyclic oligomers, in which case the relative contribution of the cyclic oligomers follows the pattern as described by Jacobson and Stockmayer²¹⁾. High yields of linear polymer can only be expected if the product formation is controlled kinetically. Regarding the formation of unwanted cyclics, it is discussed that in the case of cationic polymerization, the condensation of silanol end groups leads to predominant D_{3n} cycle formation (end-biting)^{22–25)}. Contrary to this, ring formation in anionic polymerization is caused by back-biting, resulting in formation of D_4 .

In the case of poly(di-decylsiloxane), anionic polymerization resulted in a 18% yield of relatively low-molecular-weight material (mass-average molar mass $\bar{M}_w = 36000$ g/mol, mass-average degree of polymerization $DP_w = 110$) after a total polymerization time of 45 h at 150 °C. This observation points to a decrease in the propagation rate constant k_p relative to the depolymerization rate constants k_{dx} leading to ring formation. An explanation might be given by the reduced electrophilicity of the silicon atoms within the cyclotrisiloxane ring in combination with an increase in steric hindrance between neighbouring side groups. As a result, ring formation is favoured rather than formation of linear polymer.

Although the increase in k_{dx} appeared inevitable, the inductive effect could be exploited to favour cationic polymerization, as it also affects the basicity of the oxygen atoms within the cyclotrisiloxane ring. Indeed, cationic ring opening polymerization

with trifluoromethanesulfonic acid as an initiator constituted a route to prepare high-molecular-weight poly(di-n-alkylsiloxane)s in high yields, even in the case of poly(didecylsiloxane).

Fig. 1 shows GLC diagrams of the cyclic byproducts formed during cationic ($\text{CF}_3\text{SO}_3\text{H}$, bulk, room temperature), respectively, anionic (CsOH , bulk, 150°C) polymerization of hexaethylcyclotrisiloxane. In line with observations reported before on cationic polymerization of hexamethylcyclotrisiloxane²²⁻²⁵, the cationic polymerization of cyclotrisiloxanes with longer alkyl substituents differed from anionic polymerization in the relative amount of the $\text{D}_6^{\text{Et}_2}$ byproduct. Oligomers like $\text{D}_4^{\text{Et}_2}$, $\text{D}_5^{\text{Et}_2}$, $\text{D}_7^{\text{Et}_2}$ and $\text{D}_8^{\text{Et}_2}$ (Et denoting ethyl group) were virtually absent in the cationic

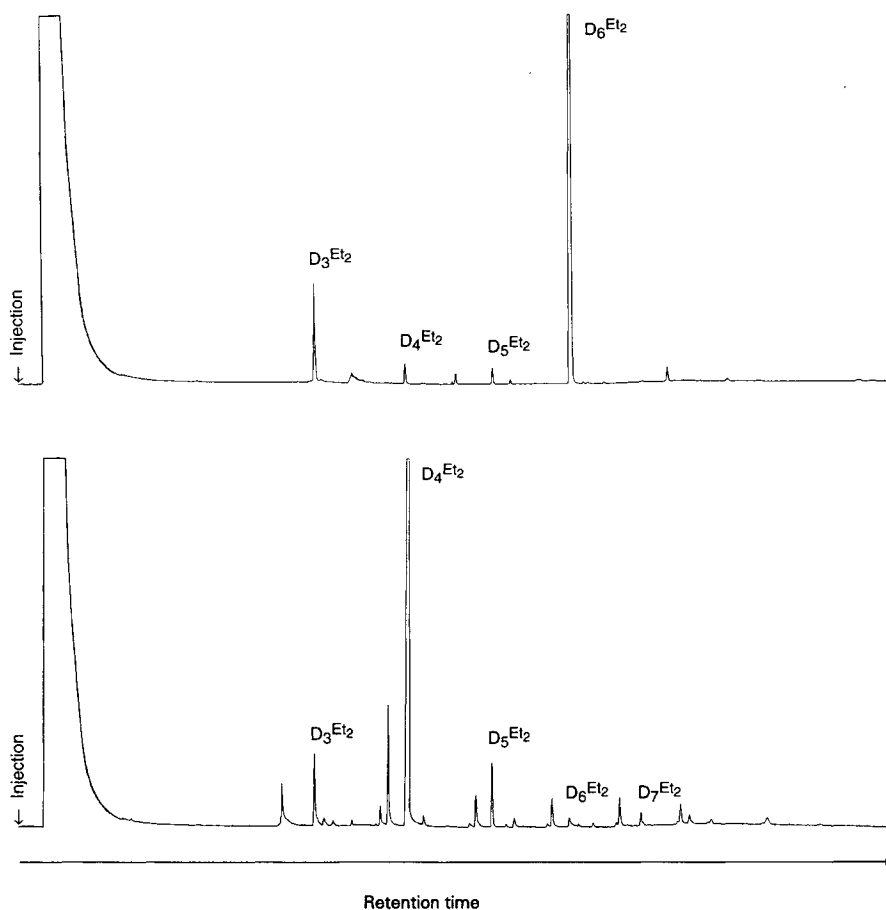


Fig. 1. Gas chromatography (GLC) traces of the cyclic byproducts in ring-opening polymerization of hexaethylcyclotrisiloxane. Top: bulk, $\text{CF}_3\text{SO}_3\text{H}$, room temperature, bottom: bulk, CsOH , 150°C

polymerization of hexaethylcyclotrisiloxane. In contrast, the anionic polymerization resulted typically in a formation of cyclic oligomers of all sizes, but with predominant formation of $D_4^{Et_2}$.

Melting behaviour of hexa-n-alkylcyclotrisiloxanes

The appearance of hexa-n-alkylcyclotrisiloxanes at room temperature varies from macroscopic transparent hexagonal plate-like crystals in case of methyl and propyl substitution, via clear colourless liquids in case of ethyl, butyl to heptyl substitution to white waxy solids in case of octyl- to decyl-substituted derivatives. Calorimetric measurements have been carried out at scan rates between 0,2 to 10 K/min and results of the measurements are summarized in Tab. 4.

Tab. 4. Melting points T_m and melting enthalpies ΔH_m and entropies ΔS_m of hexa-n-alkylcyclotrisiloxanes $(R_2SiO)_3$ as observed by differential scanning calorimetry (heating rate 5 K/min)

R	Purity in %	T_m K	ΔH_m kJ/mol	ΔS_m $J \cdot K^{-1} \cdot mol^{-1}$
methyl	99,8 ^{a)}	344	19,4	57
ethyl	99,8 ^{a)}	283	12,3	43
propyl	99,8 ^{a)}	297	30,6	103
butyl	94,3 ^{a)}	251	23,8	95
pentyl	96,9 ^{a)}	266	38,7	146
hexyl	93,4 ^{a)}	285	34,4	121
heptyl	> 98 ^{b)}	299	64,3	215
octyl	> 98 ^{b)}	313	66,1	211
nonyl	> 98 ^{b)}	317	75,0	237
decyl	92,2 ^{b)}	324	69,1	213

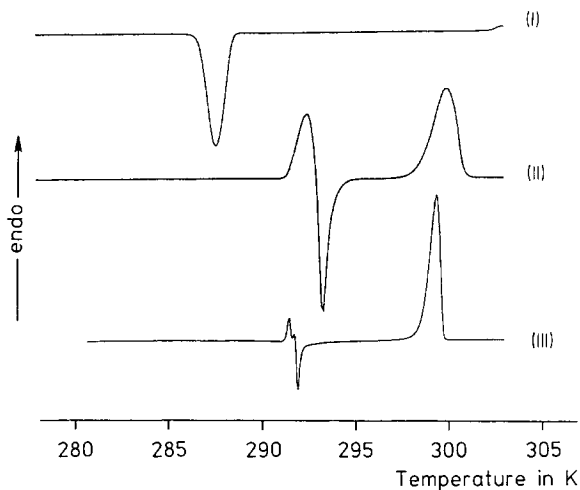
a) According to gas chromatography (GLC) analysis.

b) According to ^{29}Si NMR spectroscopy.

The first six members of the series showed only one melting transition in the differential scanning calorimetry (DSC) heating curves. Splitting of the crystallization transition into multiple transitions was frequently observed in DSC cooling traces, which might have been due to variations in crystallite size.

Cooling a sample of hexaheptylcyclotrisiloxane from the melt at a rate of 5 K/min, followed by heating at the same rate, yielded DSC curves I and II as shown in Fig. 2. Although only one crystallization transition could be observed, melting occurred via two separate transitions. The first melting transition at 292 K was immediately followed by a recrystallization peak, after which a second melting transition appeared at 299 K. Decreasing the cooling rate of 1 K/min, followed by heating at the same slow rate yielded DSC curve III (Fig. 2). Apparently, crystallization of hexaheptylcyclotrisiloxane is hindered as reflected by the large hysteresis of 10 K between the upper melting transition and the crystallization transition. At high cooling rates, this leads

Fig. 2. Differential scanning calorimetry curves of hexaheptylcyclotrisiloxane: (I) cooling at 5 K/min; (II) first heating scan at 5 K/min; (III) second heating scan at 1 K/min, after cooling at 1 K/min



to the formation of a kinetically favoured low melting crystal modification, which upon melting recrystallizes to give rise to a second melting endotherm at higher temperature.

As in case of hexaheptylcyclotrisiloxane, the melting behaviour of hexaoctylcyclotrisiloxane appeared to depend significantly on the thermal history of the sample. Fig. 3 shows the first heating scan of the material after solution crystallization (I), subsequent cooling exotherm (II) and the second heating trace (III) as obtained at a rate of 5 K/min. Although in the first heating scan, only one melting transition was observed

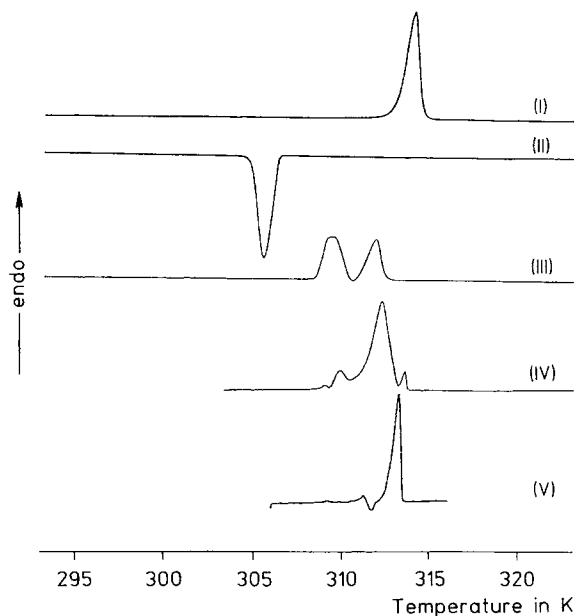


Fig. 3. Differential scanning calorimetry curves of hexaoctylcyclotrisiloxane: (I) 1st heating scan; (II) 1st cooling scan; (III) 2nd heating scan (rate 5 K/min); (IV) 3rd heating scan (rate 1 K/min); (V) 4th heating scan (rate 0.2 K/min)

at 313 K, the second heating scan showed two melting transitions at 308 K and 311 K. Cooling from the melt at 318 K at a rate of 1 K/min to 303 K, followed by heating with the same rate yielded DSC curve (IV). Only upon cooling from the melt at a rate of 0,2 K/min, the original melting transition could be observed as shown by DSC curve (V). Thus, hexaoctylcyclotrisiloxane seems to be able to form three different crystal modifications. The formation of the thermodynamically stable crystal modification is kinetically strongly hindered.

Cooling a sample of hexanonylcyclotrisiloxane from the melt at a rate of 5 K/min to 303 K, followed by heating at the same rate yielded only one crystallization transition at 315 K or melting transition at 317 K, respectively. Although both transitions were broad, reduction of the cooling rate to 0,5 K/min did not resolve different overlapping transitions. The thermal behaviour of hexadecylcyclotrisiloxane, finally, resembled that of the derivatives with shorter *n*-alkyl substituents showing only one crystallization and melting transition.

Melting enthalpies and melting entropies of the homologous series, showed higher values for the derivatives substituted by a chain with an odd number of CH₂ groups (Fig. 4).

This effect resembles the odd-even dependence known for the melting of *n*-alkanes. While in the latter case, it is well established how the dependence is related to the crystal structure, the corresponding information for the cyclotrisiloxanes is lacking. However, it might be pointed out that such an odd-even effect accounts for the methylene units per geminal alkyl group. As the silicon atoms in each case are substituted with an even total number of carbon atoms, the observed effect might derive from the crystal packing of the side groups separately.

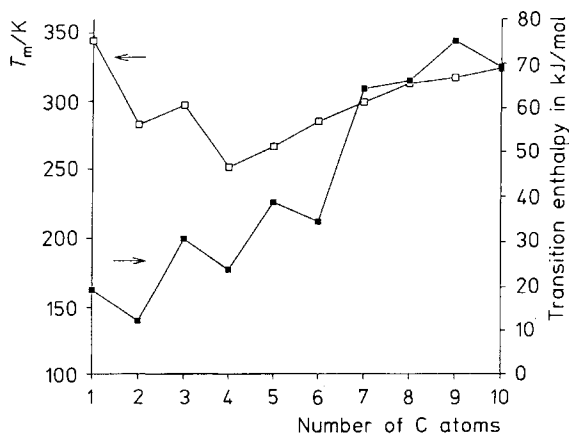


Fig. 4. Dependence of transition enthalpies and melting temperatures T_m of hexa-*n*-alkylcyclotrisiloxanes on side-group length given by number of carbon atoms

In summary, no indications have been found for a formation of mesophases. Although hexaheptylcyclotrisiloxane and hexaoctylcyclotrisiloxane displayed multiple melting transitions, it was observed that the lower melting transitions disappeared upon annealing. Consequently, the virtually planar, strained cyclotrisiloxanes, which are

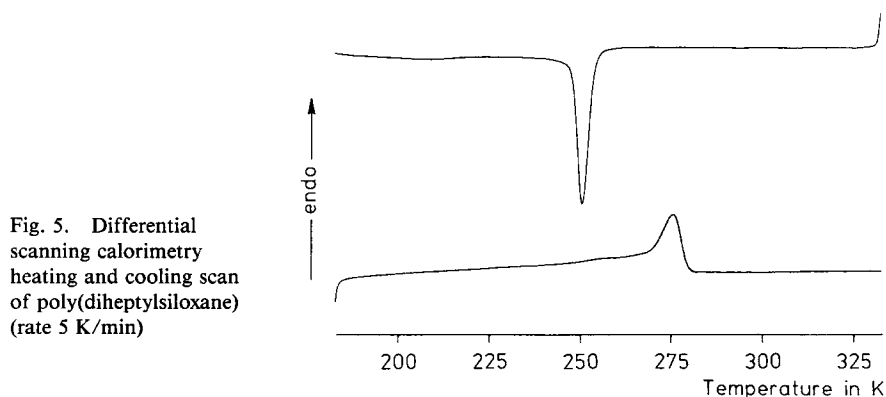
regularly substituted with *n*-alkyl side groups, do not form liquid-crystalline phases as it might have been expected for discotic-like molecules.

*Thermal behaviour of poly(di-*n*-alkylsiloxane)s*

Tab. 5 summarizes the thermal behaviour of the homopolymers as observed by DSC and optical polarizing microscopy.

Apart from poly(dimethylsiloxane), poly(diheptylsiloxane) and poly(dinonylsiloxane), all poly(di-*n*-alkylsiloxane)s are able to form two crystal phases which are separated by a first-order-like crystal-crystal transition^{a)}. By means of solid state ¹³C and ²⁹Si NMR measurements, it had been reported that within the high-temperature crystalline phase, the *n*-alkyl side groups are disordered, which yields a limited amount of motional freedom for segments of the polymer main chain as well^{6,26}. Because of the process of *conformational disordering*, this crystal phase has also been denoted as a CONDIS crystal²⁷. Apart from these two types of crystal phases polysiloxanes symmetrically substituted with ethyl to hexyl groups are also able to form a hexagonal columnar mesophase, the temperature regime of which amounted to more than 300 K in case of butyl to hexyl substituents^{12–14}. For poly(didecylsiloxane), melting of the high-temperature crystalline phase resulted in the direct transition into the isotropic melt¹⁴. Figs. 5, 6 and 7 show the thermal behaviour of poly(diheptylsiloxane), poly(dioctylsiloxane) and poly(dinonylsiloxane), respectively.

Polarizing optical microscopy revealed that poly(dioctylsiloxane) and poly(dinonylsiloxane) convert directly into an isotropic melt at 301 K and 304 K, respectively, thereby resembling the behaviour of poly(didecylsiloxane). While two different crystal-to-crystal transitions were observed for poly(di-*n*-alkylsiloxane)s with ethyl to hexyl



^{a)} So far, no pressure-volume-temperature PVT experiments could be performed to prove the first-order character unambiguously. However, it had been shown that the relation of Clausius-Clapeyron is fulfilled for the corresponding transitions of poly(diethylsiloxane) and poly(dipropylsiloxane)²⁸.

Tab. 5. Thermal behaviour of poly(di-n-alkylsiloxane)s (R_2SiO)_n as observed in differential scanning calorimetry (rate 5 K/min)

R	DP _w ^{a)}	T _g ^{b)} K	T _{dl} ^{c)} K	$\frac{\Delta H_{dl}}{kJ/mol}$ ^{d)}	$\frac{\Delta S_{dl}}{J \cdot K^{-1} \cdot mol^{-1}}$ ^{e)}	T _{d2} ^{f)} K	$\frac{\Delta H_{d2}}{kJ/mol}$ ^{g)}	$\frac{\Delta S_{d2}}{J \cdot K^{-1} \cdot mol^{-1}}$ ^{h)}	T _i ⁱ⁾ K
ethyl	1 760	135	207	2,7	13,2	283	1,8	6,5	326
propyl	1 310	163	222	3,0	13,4	334	2,2	6,6	479
butyl	2 013	157	229	3,6	15,7	254	0,9	7,6	583 ^{j)}
pentyl	3 535	167	235	9,0	38,4	254	1,9	7,6	603 ^{j)}
hexyl	6 030	—	246	3,4	13,7	296	2,2	7,3	603 ^{j)}
heptyl	18 450	—	—	—	—	268	≈ 12	≈ 45	648 ^{j)}
octyl	1 617	—	272	15,8	58,0	296	4,1	13,7	301 ^{j)}
nonyl	3 829	—	—	—	—	298	≈ 20	≈ 68	304 ^{j)}
decyl	2 750	—	286	≈ 21	≈ 72	313	≈ 9	≈ 29	320 ^{j)}

a) Mass-average degree of polymerization, based on mass-average molar mass \bar{M}_w .

b) Glass transition temperature.

c) Temperature of transition from low-temperature crystalline phase into high-temperature crystalline phase.

d) Transition enthalpy corresponding to the crystal-crystal transition.

e) Transition entropy corresponding to the crystal-crystal transition.

f) Temperature of transition from high-temperature crystalline phase into the columnar hexagonal mesophase.

g) Transition enthalpy corresponding to the crystal-mesophase transition.

h) Transition entropy corresponding to the crystal-mesophase transition.

i) Isotropization temperature.

j) Disappearance of birefringence.

Fig. 6. Differential scanning calorimetry heating and cooling scan of poly(dioctylsiloxane) (rate 5 K/min)

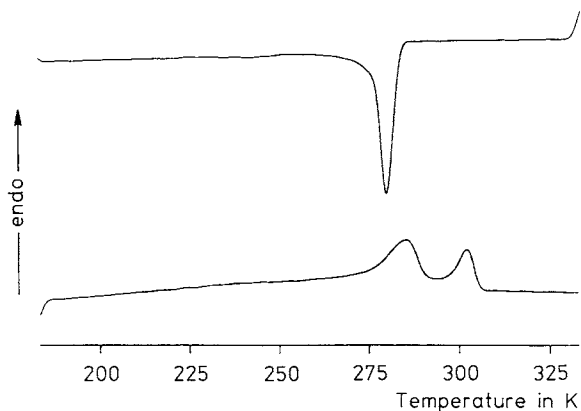
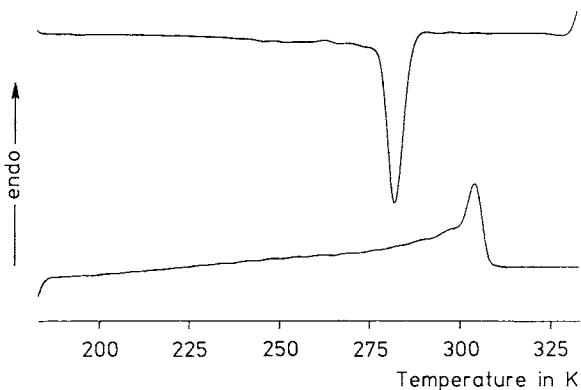


Fig. 7. Differential scanning calorimetry heating and cooling scan of poly(dinonylsiloxane) (rate 5 K/min)



side groups, broad transitions were monitored in the DSC curves of the polysiloxanes symmetrically substituted with heptyl and higher *n*-alkyl groups. Only in the case of poly(dioctylsiloxane) and poly(didecylsiloxane) a second transition was clearly separated below the isotropization transition. The broadening is even more obvious in the DSC cooling scans and might be explained by the occurrence of simultaneous crystallization of main chain and side chains, without preordering of the polymer chains in a partially ordered liquid-crystalline mesophase.

Poly(diheptylsiloxane) appeared to display peculiar birefringent behaviour. Though the material only showed weak birefringence when viewed between crossed polarizers, application of a slight pressure resulted in a large increase of the intensity. Shearing of a sample resulted in significant birefringence, which lasted until a temperature of 648 K and which could not be observed for other isotropic poly(di-*n*-alkylsiloxane)s. Unlike the behaviour of poly(di-*n*-alkylsiloxane)s with ethyl to hexyl substituents, isotropization and annealing at a temperature 50–100 °C below the isotropization temperature did not yield the characteristic band texture^{5,14}). In fact, the polymer sample had to be

cooled to 210 K before any texture reappeared at all. Examination of the ^{29}Si chemical shift anisotropy of poly(diheptylsiloxane) above the thermal transition in the heating trace depicted in Fig. 5, revealed the presence of isotropic material (Fig. 8). The absence of a partially ordered hexagonal columnar phase is confirmed by wide-angle X-ray diffraction (WAXD) experiments²⁹. Apparently, the columnar mesophase is thermodynamically unstable in case of poly(diheptylsiloxane). However, applications of a slight amount of pressure might be enough to disclose this phase state. The effect of pressure on the appearance of the WAXD patterns is currently investigated.

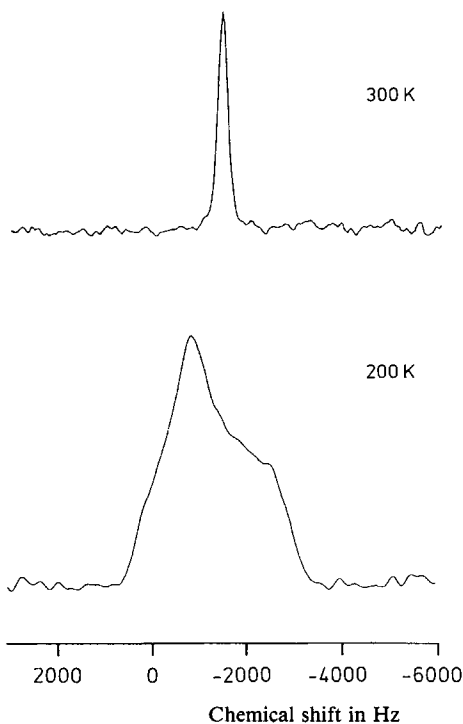


Fig. 8. ^{29}Si NMR chemical shift anisotropy of poly(diheptylsiloxane) in the crystalline phase and in the isotropic phase at 200 K and 300 K, respectively

Conclusions

The observations described in this paper indicate that poly(diheptylsiloxane) constitutes an intermediate case, which combines a stress-induced mesophase formation and a viscoelastic, rubberlike appearance under ambient conditions. The melting behaviour of poly(dioctylsiloxane) and poly(dinonylsiloxane) resemble that of poly(di-n-decylsiloxane).

Generally, the melting behaviour of poly(di-n-alkylsiloxane)s can be compared to that of the structurally similar poly(di-n-alkoxyphosphazene)s^{10, 11}. These materials have been reported to show a columnar mesophase for the propoxy-, butoxy- and pentoxy-disubstituted homologues. Substitution of the polymer backbone with longer

side groups such as heptyloxy- and octyloxy-groups resulted in preferential side-group crystallization and the absence of any columnar mesomorphic properties. The hexyloxy compound acted as an intermediate case and remained amorphous upon cooling.

The disappearance of mesophase formation upon elongation of the n-alkyl side groups has been explained by assuming that the contribution to the free energy due to side-group crystallization is so large that it governs the crystallization behaviour of the polymers, thereby preventing the formation of a columnar mesophase^{10, 11, 30)}. In this light, it is interesting to consider the columnar mesophase behaviour of poly(di-n-alkylsilylene)s⁷⁻⁹⁾, which are capable of forming a columnar-type mesophase even in case of tetradecyl substituents, although the origin of mesophase formation is considered to be similar to that of poly(di-n-alkylsiloxane)s and poly(di-n-alkoxyphosphazene)s and the side groups are even more densely packed. It might be possible that the dense substitution of the main chain in case of poly(di-n-alkylsilylene)s allows melting of the alkyl side chains into a disordered but more or less extended conformation. The entropy contribution due to melting of the side groups is thus reduced. Melting does not affect parallel alignment of the polymer molecules and the hexagonal columnar mesophase can still be formed.

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